20-119-4-27/60

AUTHORS: Ivanov, P. G., Balandin, A. A., Member, Academy of Sciences, USSR

TITLE: On the Thermal Ionization of Hydrogen and Hydrocarbons in the
           Presence of Metal Catalysts (O termicheskoy ionizatsii vodoroda
           i uglevodorodov v prisutstvii metallicheskikh katalizatorov)
                                   SSSR,
PERIODICAL: Doklady Akademii Nauk, 1958, Vol. 119, Nr 4,
           pp. 727 - 730 (USSR)

ABSTRACT: The aim of the present work is the direct detection of the
           occurrence of charged particles in the gaseous phase in the
           presence of metal surfaces with catalytic properties. The con-
           struction of the measuring apparatus is discussed on the basis
           of a schematical drawing. The device was evacuated to 10^{-4} mm
           mercury column before the experiments began. The results obtained
           by ionization tests were represented in form of time-tempera-
           ture diagrams (the abscissa stands for the time τ and the
           ordinate for temperature). The more intense ionization becomes,
           the more will the course of the curve extend towards the eye and
           downwards. A further diagram illustrates the results for hydrogen
Card 1/4   in the presence of electrodes made from palladium, aluminum and

On the Thermal Ionization of Hydrogen and Hydrocarbons $20-119-4-27/60$
in the Presence of Metal Catalysts

copper. Accordingly, the number of ions begins to increase
noticeably below 100°. It must be borne in mind that with
    an increase of temperature the ionization of hydrogen de-
pends on the material of the electrodes; it is in all cases
reproducible and reversible. Ionizability can, e.g. be charac-
terized according to that temperature at which the inverse
discharge velocity amounts to 60 seconds. The lower this amount
t_{60}, the greater ionizability will be. In palladium electrodes
this temperature is very low for hydrogen, amounting to only
$t_{60} = 90^\circ$. For palladium and aluminum electrodes it holds that
$t_{60} = 100^\circ$ and in the presence of copper electrodes it holds that
$t_{60} = 135^\circ$. In a similar manner also the ionization of the vapors
of hydrocarbons of different structure was studied: H-heptane,
$2,2,:$-trimethyl-pentane, cyclohexane; benzene; decaline, tetra-
line and also cyclic ketone; these experiments were carried out
with different electrodes. In all these cases ionization occurred.
Experiments carried out with hydrocarbons were reproducible
with the exception of cases with hysteresis. Also in this case

Card 2/4

On the Thermal Ionization of Hydrogen and Hydrocarbons   2o-119-4-27/6o
in, the Presence of Metal Catalysts

the ionization observed depends in a high degree on the elec-
trode material and therefore occurs on the surface of the metal.
Besides, such an ionization depends on the nature of the gas, and
therefore it occurs on the layer of molecules adsorbed on the
gas. On the electrodes the electrons rapidly enter into the me-
tal, and therefore there is no equilibrium in ionization under
the conditions described. In tetraline and decaline there may
be a hysteresis because of the presence of a steric factor. The
sequence found here is parallel to that of the catalytic activi-
ty of the metals in hydrogenization and dehydrogenization. The
phenomenon found here develops within the same intervals of tem-
perature as also the catalytic reactions mentioned. The new
effect proved to. exist here is important for catalysis. It is
not taken into account by hitherto developed electron theories
of catalysis, but this must, without doubt, be done in the case
of a further development of the theory. The investigation is
continued.   There are 4 figures, 1 table and 2 references, none of
which are Soviet.

Card 3/4

On the Thermal Ionization of Hydrogen and Hydrocarbons   20-119-4-27/60
in.the Presence of Metal Catalysts

ASSOCIATION: Moskovskiy gcsudarstvennyy universitet im. M. V. Lomonosova
             (Moscow State University imeni M. V. Lomonosov)

SUBMITTED: December 26, 1957

Card 4/4

AUTHORS: Balandin, A. A., Member, Academy of Sciences, USSR.
                Bogdanova, O. K., Shcheglova, A. P.

TITLE: The Production of Isoprene by Catalytic Dehydrogenation
                of Isopentenes
                (Polucheniye izoprena putem kataliticheskoy degidrogenizat-
                sii izopentenov)

ABSTRACT: This synthetic production in connection with the polyme-
                rization of isoprene and the production of isoprene-rub-
                ber with better properties than natural rubber makes the
                method of isoprene production a problem of topical inter-
                est. Cheapest and most promising are mineral oil and its
                derivatives as raw material. The mineral-oil industry
                disposes of considerable supplies of isopentane and iso-
                pentenes which can be utilized for the above-mentioned
                purpose by the method mentioned in the title. The con-
                ditions of reaction according to publications (References
                1-4) are given. For determining the optimum conditions
Card 1/2   the authors investigated this reaction at different tem-

The Production of Isoprene by Catalytic Dehydrogenatio. SOV/20-120-2-19/63
of Isopentenes

peratures and supply velocities of isopentenes as well
as by different dilution with steam. The results are
given in table 1 and figures 1-3. The best conditions
for the dehydrogenation of isopentenes to isoprene are:
temperature 580-620°C, supply velocity per 1 liter cata-
lyst 5000-8000 ml/hour, and dilution with steam 1 : 2,3-3.3
(by weight). The catalyst does not need regeneration for
a longer period of time. Experiments of results were also
made at 600°C and supply velocities of 6700-7200 ml/liter/
hour as well as a steam dilution of 1 : 3. The results
are given in table 2. Finally the kinetics of the reac-
tion was investigated and a velocity constant of 4,3
ml/min at 530°C and 12,25 ml/min at 590°C was determined.
The activation energy of the reaction is equal to 23,3
Koal/mol.
There are 3 figures, 2 tables, and 5 references, 1 of
which is Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo
Akademii nauk SSSR (Institute of Organic Chemistry imeni
N. D. Zelinskiy, AS USSR)

SUBMITTED: March 7, 1958

Card 2/2   1. Isopentenes--Dehydrogenation   2. Isopentenes--Polymerization
3. Synthetic rubber--Production   4. Mineral oils--Applications

AUTHORS: Balandin, A. A., Member, Academy of   SOV/20-120-4-24/67
             Sciences, USSR, Sovalova, L. I., Slovokhotova, T. A.

TITLE: Catalytic Transformations of 2-Methyl-Thiophene Under Steam
             Influence (Kataliticheskiye prevrashcheniya 2-metiltiofena
             pod vliyaniyem parov vody)

ABSTRACT: Difficulties were bound to occur in connection with the prob-
             lem of the applicability of the reaction of the catalytic de-
             methylation to the thiophene derivatives because of the spe-
             cific behaviour of the latter on metallic catalysts in the
             presence of hydrogen (Refs 6-11) which is known to be a pro-
             duct of the said reaction. Ni/Al_2O_3 and Co/Al_2O_3 were used as
             catalysts. The velocity and the products of the reaction of
             2-methyl-thiophene with water change gradually if its vapors
             are allowed to pass above a fresh catalyst (Fig 1, Table 1).
             2-methyl-thiophene separates the methyl group and is subjected
             to a small extent to a ring cleavage. The existence of lateral
             methyl groups renders the ring system more reactive. During the
Card 1/3   first minutes of the experiment the liquid catalyzed product

Catalytic Transformations of 2-Methyl-Thiophene   SOV/20-120-4-24/67
Under Steam Influence

contains thiophene which vanishes as soon as the velocity of
the gas separation has attained a constant value. The quantity
of CO_2 first exceeds that of the saturated compounds, vanishes
then, however, together with thiophene. Unsaturated hydrocar-
bons and H_2S occur at temperatures higher than $400°$. The co-
catalyst has an effect similar to that of Al. Table 2 shows
the dependence of the composition of the liquid and gaseous
products on the temperature, on the quantity of water, and on
the composition of the catalyst in the experiment with methyl-
thiophene. Within 1 hour of heating in hydrogen the consumed
catalyst is restored, unless it had lost its activity completely
before. A longer heating increases its activity (Table 3).
Her e from it can be concluded that methyl-thiophene is demethy-
lated in the reaction in question. The complete cleavage of the
methyl-thiophene molecule which occurs as well may develop with
the participation of either hydrogen or water. The dealkylation
of methyl-thiophene thus determined is a model reaction for the
production of thiophene from alkyl substituted. The present

Card 2/3   paper in principle shows a possibility of obtaining accessible

Catalytic Transformations of 2-Methyl-Thiophene   SOV/20-120-4-24/67
Under Steam Influence

          raw material for the synthesis on thiophene basis from sul-
furous mineral óils and slate resins (Ref 12). The reaction
can be carried out on a mobile contact mass with a con-
tinuous regeneration of the circulating catalyst. There are
2 figures, 3 tables, and 19 references, 12 of which are Soviet.

SUBMITTED: February 18, 1958

       1. Thiophene aldehydes--Catalysis   2. Metal catalysts--Chemical
effects

Card 3/3

21(8), 5(4)

AUTHORS: Balandin, A. A., Academician,   SOV/20-121-3-28/47
             Dobrosel'skaya, N. P., Mikhaylenko, I. Ye., Spitsyn, Vikt.I.,
             Academician

TITLE: Radioactive Catalysts (Radioaktivnyye katalizatory) The
             Dehydration of Cyclohexanol Over the Sulphates of Magnesium
             And Sodium(Degidratatsiya tsiklogeksanola nad sul'fatami
             magniya i natriya)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 121, Nr 3,
             pp 495 - 498 (USSR)

ABSTRACT: Some recent investigations used the irradiation by γ-rays
             or neutrons for the influencing of the processes of hetero-
             geneous catalysis. In the present paper, however, the catalyst
             itself is used as a source of the ionizing radiation for the
             heterogeneous catalysis of gaseous substances. This cata-
             lyst contained various quantities of the radioactive iso-
             tope (β-radiator). It is assumed that the continuous bom-
             bardment by β-particles will energetically influence the
             processes which occur on the boundary solid body-gas. There
Card 1/4   may be also an influence of the radiation on the structure

Radioactive Catalysts. The Dehydration of Cyclo-   SOV/2o-121-3-28/47
hexanol Over the Sulphates of Magnesium and Sodium

of the catalyzer (especially a change of the properties
of its surface) and a radiation—chemical influence of
radiation on the gaseous reagents even before their
contact with the catalyzer. The object of the investigation
was the catalytic dehydration of cyclohexanol over the
sulphates of magnesium and sodium, in which the sulphur
was substituted by various quantities of radioactive
sulphur S^{35}. The investigation was carried out by
means of a catalytic apparatus of the flowing type with an
inserted reactor. This apparatus was placed in a tubular furnace
with automatic feeding. The radioactive preparations $MgSO_4$

and the measurement of the radioactivity of the catalysts
are then discussed.No gaseous products were generated by this
reaction. The apparatus did not indicate the presence of
any radioactive contaminants. The more non-radioactive
sodium sulphate is added to the magnesium sulphate , the
more does catalytic activity decrease. Also anhydrous sodium
sulphate is a catalyzer for the dehydration of cyclohexanol,
Card 2/4   although it is rather less active than magnesium sulphate.

Radioactive Catalysts. The Dehydration of Cyclo-   SOV/20-121-3-28/47
hexanol Over the Sulphates of Magnesium and Sodium

The degree $\triangle$ of the conversion of cyclohexanol into
cyclohexene increases with an increase of the radioactivity
of the catalyst, but these increases are not proportional
which respect to one another. The Arrhenius (Arrenius)
equation can be applied to the cases discussed in this
paper. The paper showed experimentally that the radie-
active radiation of the catalyst has an influence on cata-
lytic activity and on activation energy. Finally, some
possible explanations of the results of this paper are
discussed. The discussed phenomena are a completely new
effect of simultaneous action of the electrons and active
centers of the catalyst. It may be assumed that the β-
particles act upon the catalytically active centers which
had adsorbed cyclohexanol molecules. The β-particles
diminish the activation energy of the dehydration of
cyclohexanol. Investigations are being continued. There
are 4 figures, 1 table, and 8 references, 5 of which are
Soviet.

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Radioactive Catalysts. The Dehydration of Cyclo-   SOV/20-121-3-28/47
hexanol Over the Sulphates of Magnesium and Sodium

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im.M.V.Lomonosova
                (Moscow State University imeni M.V.Lomonosov)
                Institut fizicheskoy khimii Akademii nauk SSSR (Institute
                of Physical Chemistry, AS USSR)

SUBMITTED: April 23, 1958

Card 4/4

AUTHORS: Nazarova, N. M., Balandin, A. A.,   SCV/20-121-5-28/50
              Member, Academy of Sciences, USSR, Freidlin, L. Kh.

TITLE: Catalytic Alkylation of n-Butane by Means of Ethylene at High
              Temperatures and High Pressures (Kataliticheskoye
              alkilirovaniye n-butana etilenom pri vysokikh temperaturakh
              i davleniyakh)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 121, Nr 5,
              pp. 865-868 (USSR)

ABSTRACT: The authors already previously found (Refs 1 - 3) that a cata-
              lytic alkylation of normal paraffin hydrocarbons by olefins
              is possible at increased temperatures (450°), and increased
              pressure (500 atmospheres of excess pressure). This work is a
              continuation of those referred to above. The tests were
              carried out under flow conditions. The equipment, the methods
              of both test and analyses have been described already pre-
              viously (Ref 1). The results have shown that the reaction re-
              ferred to in the title yields a complicated mixture of hydro-
              carbons. The expected hexane fraction (affiliation product of
              butane to ethylene) was more considerable than the other

Card 1/3

Catalytic Alkylation of n-Butane by Means of   SOV/20-121-5-28/50
Ethylene at High Temperatures and High Pressures

fractions of the alkylate, whereas the number of their double
bonds was considerably smaller than that of other fractions.
Table 1 gives the test results, yields of alkylates and the
characteristic of the obtained fractions. Approximately one
half (51,8 volume percent) could be distilled off up to 125°.
It follows from the test results that ethylene is mainly af-
filiated to the 2nd C-atom of butane and that it forms
3-methyl pentane. There is less affiliation to the first
C-atom and n-hexane is formed. During the alkylation hydro-
carbons boiling at higher temperatures are also formed be-
sides those to be expected. It could be assumed that they are
mainly products obtained by a re-alkylation of the developed
3-methyl pentane (Fig 1,II). The affiliation in this stage,
however, takes place mainly to the first and not to the 2nd
C-atom. Yu.P. Yegorov and G.K. Gayvoronskaya have recorded
the spectra of the fraction and deciphered them. A.I. Faliy
and V.N. Zharov took part in this work.
There are 2 figures, 2 tables, and 7 references, 5 of which
are Soviet.

Card 2/3

Catalytic Alkylation of n-Butane by Means of   SOV/20-121-5-28/50
Ethylene at High Temperatures and High Pressures

ASSOCIATION: Institut organicheskoy khimii im. N.D. Zelinskogo Akademii
                nauk SSSR (Institute of Organic Chemistry imeni N.D.
                Zelinskiy, AS USSR)

SUBMITTED: April 26, 1958

Card 3/3

AUTHORS: Balandin, A. A., Member, Academy of   SOV/2o-122-2-17/42
            Sciences, USSR, Karpeyskaya, Ye. I., Tolstopyatova, A. A.

TITLE: Investigation of the Catalytic Dehydrogenation of
            Hydrocarbons and Alcohols Over Metallic Rhenium (Issledovaniye
            kataliticheskoy degidrogenizatsii uglevodorodov i spirtov
            nad metallicheskim reniyem)

ABSTRACT: In recent years more attention has been given to the
            investigation and the use of rhenium above all to
            the determination of its catalytic properties. The
            authors extended their investigations beyond the subject
            mentioned in the title (a review Ref 1). According to
            the multiplet-theory of catalysis a lattice of the
            catalyst of the A1 or A3-type and an atomic radius
            r within a range of from 1,22 to 1,39 Å is necessary
            for the dehydrogenation of the sextet-type (Ref 2).
            Later it was known that metallic rhenium has an A3-lattice
            and an atomic radius of 1,368 $\overset{o}{\text{Å}}$. Thus, it corresponds
Card 1/3   to the above requirements and must theoretically be able

Investigation of the Catalytic Dehydrogenation of Hydro-   SOV/20-122-2-17/42
carbons and Alcohols Over Metallic Rhenium

to dehydrogenate catalytically 6-membered hydro-
carbons. The structure and the atomic radius of rhenium
satisfy the principle of the maintenance of the valent
angle of the multiplet-theory (Refs 3,4); for this
reason rhenium may also serve as catalyst for the
dehydrogenation of hydrocarbons and alcohols according
to the doublet-mechanism. The mentioned catalytic
properties were experimentally only insufficiently in-
vestigated (Refs 5,7,8). Above all, the experimental
details as well as the method of production of the
catalyst are unknown. For this reason the authors made
the present investigations. It was proved by the authors
that rhenium applied on coal yields an active catalyst of
dehydrogenation of cyclohexane and its homologs, cumene,
as well as of the dehydrocyclization of n-heptane. On
the rhenium catalysts produced by the authors also
alcohol-dehydrogenation takes place between 120 and 300°
as well as the conversion of butane-diol-1,4 into γ-
butyrolactone. There are 4 tables and 13 references,
9 of which are Soviet.

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Investigation of the Catalytic Dehydrogenation of Hydro-   SOV/20-122-2-17/42
carbons and Alcohols Over Metallic Rhenium

ASSOCIATION: Institut organicheskoy khimii im. N.D.Zelinskogo Akademii
               nauk SSSR (Institute of Organic Chemistry imeni N.D.
               Zelinskiy, AS USSR)

SUBMITTED: July 16, 1958

Card 3/3

5(3)

AUTHORS: Balandin, A. A., Academician,   SOV/20-123-1-21/56
Khidekel', M. L.

TITLE: The Kinetics of the Catalytic Hydrogenation of Molecules
as Related to Their Structure (Struktura molekul i kinetika
ikh kataliticheskoy gidrogenizatsii)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 123, Nr 1,
pp 83 - 86 (USSR)

ABSTRACT: The influence of substituents on the atoms, the linkages
of which are subject to catalytic hydrogenation, upon
the rate of this reaction has repeatedly been studied.
This influence is due to steric as well as to energy
factors which are coupled with each other. The present
paper deals mainly with such cases in which the energy
factors are predominant. The authors have investigated
the hydrogenation kinetics of typical representatives
of compounds with aromatic and conjugated bonds (in
particular of such which differ with regard to σ). The
purpose was to study the effect of σ upon v (σ is the
conjugation energy, Refs 6,7). The following substances

Card 1/5

The Kinetics of the Catalytic Hydrogenation of   SOV/..o-125-1-21/56
Molecules as Related to Their Structure

were investigated: benzene, pyridine, pyrrole, furan
and some of its derivatives, cyclohexadiene-1,4 and-1,3,
dihydrofuran-3,4, cyclopentadiene, cyclopentene,
eugenol as well as cis and trans iso-eugenol. The order
of reaction as determined by a modification of con-
centration in a broad range, was equal to zero for all
the mentioned compounds. In tables 1-3 the results
obtained are presented which permit the following con-
clusions: 1) By the increase of the conjugation energy
of the compounds undergoing hydrogenation the rate
constant k is reduced. 2) The conclusion (4) from
equation (3)

$$\delta E = -\delta_{Q_{C_1}} = c + \delta_{Q_{C_1}K} - r\delta \quad (3)$$

$$\delta u = -\delta_{Q_{C_1}} = c + \delta_{Q_{C_1}H} - \delta\sigma \quad (4)$$

elucidates the activation of the cyclopropane ring
by introduction of the phenyl group into the conjugation
Card 2/5   with this ring (Table 2, d) (investigated by B.A.Kazanskiy

The Kinetics of the Catalytic Hydrogeration of   SOV/2o-123-1-21/56
Molecules as Related to Their Structure

and coworkers, Refs 8,9). The activating effect
of the conjugation in other cases can be equally ex-
plained (Ref 22). 3) The influence exerted by the
substituents at their introduction upon the rate
constant (Table 3) shall be explained by the action
of the induction and hyperconjugation effects on $Q_{C_1=C}$, Q_{CK}

and Q_{CH} (equation 3) as well as by steric factors. 4)
The modification of temperature does not interfere with
the principle mentioned in 1) for compounds considerably
differing regarding σ, this rule might, however, be
disturbed in the case of closely neighboring σ values,
because the dependence of the adsorption coefficients
of the compounds to be compared on the temperature is
unequal (Table 2). 5) A considerable variation of the
chemical nature of the bonds to be hydrogenated is also
capable of interfering with the rule of 1), in
correspondence with equation (3). The σ values for pyrrole

Card 3/5   and benzene for instance, are in close neighborhood although

The Kinetics of the Catalytic Hydrogenation of   SOV/20-123-1-21/56
Molecules as Related to Their Structure

χ is smaller for pyrrole than for benzene (Refs 18,21).
This may be explained by the interaction of the nitrogen
atom which possesses an undivided pair of electrons
with a surface Rh. 6) The analysis of the results
obtained and of those of reference 23 shows that in
ge.eral the influence exercised by the solvent is not
strong enough to vary the principle of 1) at a con-
siderable difference of the σ values. 7) It can be
seen from table 1 and 2 that the activation energy
is not affected by the conjugation energy (according to
the result of reference 13 concerning Pt). 8) Most
of the obtained results (Tables 1 and 2) are sufficiently
described by the ratio

$$\lg \frac{k_1}{k_2} = a(\sigma_2 - \sigma_1) + b$$ which has previously not been

known. k_1 and k_2 are the observed rate constants of the
hydrogenation of both compounds to be compared, σ_1 and σ_2 -

Card 4/5   their conjugation energies, a and b - constants (Fig 1).
There are 1 figure, 3 tables, and 26 references, 13 of which

The Kinetics of the Catalytic Hydrogenation of   SOV/2o-123-1-21/56
Molecules as Related to Their Structure

      are Soviet.

ASSOCIATION: Institut organicheskoy khimii im.N.D.Zelinskogo Akademii
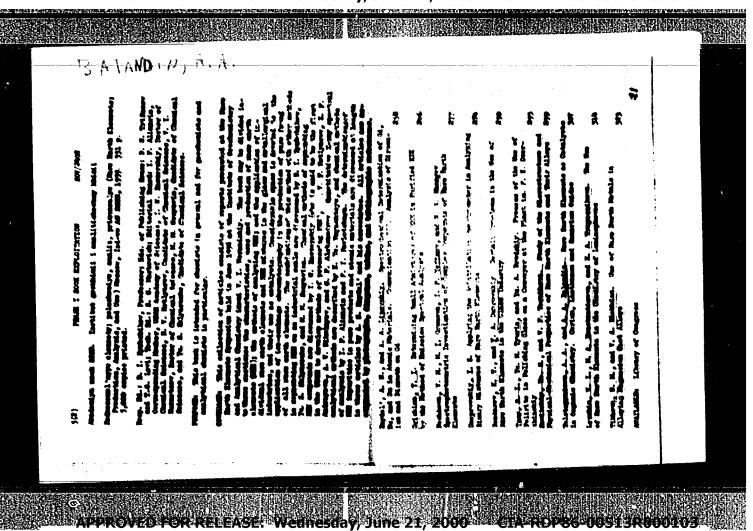   nauk SSSR (Institute of Organic Chemistry imeni N.D.
             Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: August 5, 1958

Card 5/5

5(4)

AUTHORS: Balandin, A. A., Sokolova, N. P.   SOV/62-59-2-5/40

TITLE: On Catalytic Properties of Tungsten Bronzes (O kataliticheskikh
             svoystvakh vol'framovykh bronz)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
             1959, Nr 2, pp 214-224   (USSR)

ABSTRACT: In the present paper an attempt was made to clarify the
             problem of the catalytic activity of tungsten bronzes. The
             catalytic properties of Na-W-bronzes were investigated in
             comparison with the corresponding activity of tungsten an-
             hydride and para tungstate. It could be found that the
             Na-W-bronzes are catalytically little active compounds. Bronzes
             catalyze the dehydration of isopropyl alcohol and with small
             yield only the decomposition of ethyl alcohol. Formic acid
             is mainly dehydrated and partly dehydrogenated. With regard
             to the dehydrogenation of cyclohexane and piperidine, to the
             reduction of nitrobenzene and to the oxidation of toluene the
             Na-W-bronzes are catalytically passive. The catalytic
             activity of bronzes is less than the corresponding activity
             of WO_3 and tungstate. It decreases on the transition of

Card 1/3   bronze to bronze according to the degree of its reduction and

On Catalytic Properties of Tungsten Bronzes   SOV/62-59-2-5/40

also on addition of lithium. Some parallelism was found
between the catalytic activity and the degree of lattice
defects of bronzes. This is in accordance with the electron
theory of the catalysis (Refs 13,30) the small catalytic
activity of the lattice defects is, however, on the other hand
in contradiction to this theory. Though the lattice defects
support catalysis, they are by no means the only prerequisite
for the catalytic activity. In addition to the defects also
steric and energetic relations will have to be considered.
The X-ray structure analysis was carried out by Yu. P. Simanov
in the X-ray Laboratory of the Chemistry Department at the
MGU, the adsorption analysis by A. Ye. Agronomov, holding the
Chair of Organic Catalysis MGU. Electron diffraction studies
were performed by M. I. Dashevskiy in the laboratory of
A. M. Rubinshteyn in the IOKh AS, USSR. The authors expressed
their gratitude to them. There are 2 figures, 6 tables, and
30 references, 12 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii
                nauk SSSR (Institute of Organic Chemistry imeni N. D.
Card 2/3   Zelinskiy of the Academy of Sciences, USSR)

.5(3)   SOV/62-59-2-27/40
AUTHORS: Bogdanova, O. K., Shcheglova, A. P., Balandin, A. A.

TITLE: Catalytic Dehydrogenation of Isopentane-Isopentene Mixtures
                (Kataliticheskaya degidrogenizatsiya izopentan-izopentenovykh
                smesey)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
                1959, Nr 2, pp 350-352 (USSR)

ABSTRACT: In this news in brief the authors report on the dehydrogenation
                of isopentane-isopentene mixtures by means of the continuous
                flow method in a device described in reference 1. The results
                obtained showed that the dehydrogenation of isopentane-iso-
                pentene mixtures can be carried out on the "chromo-aluminum"
                catalyst by dilution with steam. Optimum conditions are:
                600-620°, flow rate 5000-6000 ml/1 per hour, dilutions with
                steam in a weight ratio of 1:3. Under these conditions the
                yield of isoprene is 38-40% of the initial isopentenes and
                88-92% of the reacted mixture. The high yield of isoprene
                indicates that no decomposition of hydrocarbons takes place
                under the influence of steam. The catalyst is distinguished by
Card 1/2   a considerable selectivity and is able to operate for some time

SOV/62-59-2-27/40

. Catalytic Dehydrogenation of Isopentane-Isopentene Mixtures

without regeneration. The mixtures used were produced in the
laboratory of B. A. Kazanskiy and N. I. Shuykin.
There are 1 figure, 3 tables, and 3 references, 2 of which
are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii
nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy
of the Academy of Sciences, USSR)

SUBMITTED: July 4, 1958

Card 2/2

5(3)

AUTHORS: Balandin, A. A., Khidekel', M. L., Patrikeyev, V. V. SOV/62-59-2-33/40

TITLE: On the Catalytic Hydrogenation of the Free Radical of 1,1-Di-
phenyl-2-picryl Hydrazyl on the Rhodium Catalyst (O
kataliticheskom gidrirovanii svobodnogo radikala 1,1-difenil-2-
pikrilgidrazila - na rodiyevom katalizatore)

ABSTRACT: It was found in the present paper that the hydrogenation of
1,1-diphenyl-2-picryl hydrazyl (I) proceeds systematically
wherein the saturation of the radical is the first stage:

Furthermore the hydrogenation of the polynitro compound, the di-
phenyl picryl-hydrazine takes place, which was, however, not
investigated in detail. The systematic course of hydrogenation
was determined by titration with acetic acid hydroquinone solu-

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On the Catalytic Hydrogenation of the Free Radical of 1,1-Diphenyl-2-picryl Hydrazyl on the Rhodium Catalyst

SOV/62-59-2-33/40

tion. It was found that first the radical is hydrogenated. The systematic course of hydrogenation of (I) becomes particularly evident on the potential curve (Fig 1, below) and less distinct on the kinetic curve (Fig 1, above). The effect of the con- centration of (I), temperature and the quantity of the catalyst on the reaction rate was investigated. It was found that the hydrogenation of (I) proceeds according to an equation of the order zero. The low hydrogenation rate of 1,1-diphenyl-2-picryl hydrazine is explained by a considerable amount of its conjuga- tion energy which is due to a displacement of the free electron. The conjugation energy must be taken into account when using energy equations of the multiple theory (Ref 8) as well as in the investigation of the influence exerted by the structure upon the rate of catalytic hydrogenation. There are 2 figures and 8 references, 4 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

Card 2/3

5(3)

AUTHORS:

SOV/62-59-2-34/40

Vasserberg, V. E., Balandin, A. A., Maksimova, M. P.

TITLE: Orientation of Adsorbed Molecules in the Monomolecular Layer on Oxidizing Catalysts (Ob oriyentatsii adsorbirovannykh molekul v monomolekulyarnom sloye na okisnykh katalizatorakh)

ABSTRACT: In the present paper the authors investigated the adsorption of the lowest saturated alcohols, from C_1 to C_4, of n-pentane and dichloro ethane by differently produced Al_2O_3 -samples and MgO-, ThO_2- and ZnO-catalysts. From the determinations of the adsorption isothermal lines at 25^0 it was seen that the adsorption in the monomolecular layer is decreasing in the following order: $CH_3OH > C_2H_5OH > n-C_3H_7OH > n-C_4H_9OH > i-C_3H_7OH = i-C_4H_9OH > s-C_4H_9OH > t-C_4H_9OH$. The size of the elementary places occupied by the adsorbed alcohol molecules on the surface depends both on the structure of the alcohol and on the catalyst. It was assumed that at moderate temperature

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Orientation of Adsorbed Molecules in the Monomolecular Layer on Oxidizing
Catalysts

there is also a plane orientation in addition to the normal
one of the adsorbed molecules (hydroxyl groups are oriented
towards the surface). The portion of planely oriented molecules
is different for various alcohols and catalysts. For this
reason it is advisable to introduce instead of the actual size
of the elementary place a new term, the "effective specific
place" σ_{eff}. It depends on the numerical ratio of the planely
and parallelly adsorbed molecules and is different for one and
the same alcohol on various catalysts. The variation of the
chemical character of the catalyst considerably affects the
σ_{eff}. (Table). There are 1 table and 9 references, 6 of which
are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii
nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy
of the Academy of Sciences, USSR)

SUBMITTED: July 15, 1958

Card 2/2

5(2)

AUTHORS: Balandin, A. A., Sokolova, N. P.

SOV/62-59-5-39/40

TITLE: Letters to the Editor (Pis'ma redaktoru). On the Condensing Pro-
              perties of Niobium- and Tantalum-oxides (O kondensiruyushchikh
              svoystvakh okislov niobiya i tantala)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
              1959, Nr 5, pp 949 - 950 (USSR)

ABSTRACT: In the course of the further development of an investigation
              dealt with by an earlier paper (Ref 1), the present paper inves-
              tigates the ability of niobium- and tantalum oxides of catalysing
              the condensation reaction on the basis of the example of the
              formation of croton aldehydes from acetaldehyde in the vaporous
              phase. It was found that both the Nb- and the Ta-oxides, in
              contrast to Al_2O_3-catalysts, act as selective condensation cata-
              lysts. The investigations were carried out by means of a con-
              tinuous-flow apparatus. With a rate of flow of the acetaldehyde
              passing through of 0.10-0.15 ml/min and at a temperature of
              336-340° a maximum yield of croton aldehyde was obtained. As cata-
              lysts the Nb- and Ta-oxides were used in pure form, singly, and
              in form of a mixture of both asbestos and carbon and with the
Card 1/2   addition of acid and basic substances such as SiO_2, Al_2O_3, CaO

Letters to the Editor. On the Condensing Properties of   SOV/62-59-5-39/40
Niobium- and Tantalum-oxides

and BaO. The manner in which the catalyst is produced influences
its catalysing ability considerably. The highest degree of acti-
vity was found in Nb_2O_5 on asbestos, which had been produced from
the oxalate complex of niobium (1 $Nb_2O_5:2H_2C_2O_4$). The croton al-
dehyde yield amounted to 30% of the acetaldehyde allowed to pass
through. The data of the croton aldehyde obtained are: boiling
point 102.5-104°, n_D^{20} 1.4370. There is 1 Soviet reference.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk
SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of
the Academy of Sciences, USSR)

SUBMITTED: March 14, 1959

Card 2/2

5(4)   SOV/62-59-6-7/36
AUTHORS: Balandin, A. A., Khidekel', M. L., Patrikeyev, V. V.

TITLE: Adsorption and Catalysis (Adsorbtsiya i Kataliz).Communication
                2. Reaction Rate, Surface Potential, and Adsorption Correlation
                During Hydration (Soobshcheniye 2. Skorost' reaktsii, pote..t-
                sial poverkhnosti i adsorbtsionnyye sootnosheniya pri gidriro-
                vanii)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
                1959, Nr 6, pp 999 - 1004 (USSR)

ABSTRACT: In a previous paper (Ref 1) a mutual influence of maleic- and
                fumaric acid exercised upon adsorption and hydration could be
                observed. In this connection, the kinetic- and adsorption inter-
                action of the two aforementioned acids, was subjected to closer
                investigation by the present paper. The potentiometric method
                was applied for investigating the hydration reaction in the
                circulation system. Catalysts were used which adsorbed either
                both or only one of the acids. By means of these catalysts the
                intensity with which the acids were adsorbed from the mixture,
                and the rate of their catalytic transformation were determined.
Card 1/3   The intensity of the hydration reaction depended on the fraction

Adsorption and Catalysis. Communication 2. Reaction   SOV/62-59-6-7/36
Rate, Surface Potential, and Adsorption Correlation During Hydration

of the component which occupied the surface of the catalyst
(stopped after 50% hydration and measured; table 1). The cha-
racteristics of the catalysts used are given in table 2. Accord-
ing to these experiments, the volume-, the specific-, and the
real hydration rate was calculated for the two acids (Table 3).
An addition of thiophen to the mixture of the acids decreased
their hydration to zero. The strong adsorption of maleic acid
which occurs in this case also decreased the adsorption of
fumaric acid. Nevertheless, the potential of the catalyst as
compared to that of the mixture of the acids decreased only
slightly. A parallelism could be observed between the potential
drop of the mixture of the acids and their adsorption. The ex-
perimental results on the adsorption- and kinetic interaction
obtained in the course of the investigation dealt with by the
paper under review are in good agreement with the theoretical
description of the hydration by Balandin (Ref 6). There are 4
figures, 5 tables, and 6 references, 4 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk
               SSSR(Institute of Organic Chemistry imeni N. D. Zelinskiy of

Card 2/3   the Academy of Sciences, USSR)

Adsorption and Catalysis. Communicatior 2. Reaction   SOV/62-59-6-7/36
Rate, Surface Potential, and Adsorption Correlation During Hydration

SUBMITTED: August 22, 1957

Card 3/3

5 (3)

'AUTHORS: Balandin, A. A., Khidekel', M. L.,   SOV/62-59-7-4/38
             Patrikeyev, V. V.

TITLE: Adsorption and Catalysis (Adsorbtsiya i kataliz). Communication 3.
             Successive Hydrogenation of Cyclopentadiene (Soobshcheniye 3.
             Posledovatel'naya gidrogenizatsiya tsiklopentadiyena)

ABSTRACT: For studying the adsorption- and kinetic interrelation of the
             reacting substances, the reaction of the successive hydrogenation
             of the cyclopentadiene (I) is investigated in this paper,
             running according to the following scheme:

             This reaction is a characteristic one because it represents the
             critical case of the hydrogenation of a binary mixture in which
             the interrelations of the individual reaction participants are
             perceptible. The adsorption and hydrogenation were investigated
             in a circulating system which was developed in the paper
Card 1/4   mentioned in reference 1. Catalyst and (I) were renewed after

Adsorption and Catalysis. Communication 3. Successive   SOV/62-59-7-4/38
Hydrogenation of Cyclopentadiene

every performed experiment. Furthermore the same investigations
were carried out with cyclopentene (II) to illustrate the
process. In figures 1, 2, 3 the kinetic and potential hydrogenation
curves of (I), (II) and of a mixture of these are given. It
becomes evident that the hydrogenation of (I) takes place much
quicker and at lower potentials than that of (II). Both reactions are
of the zero order. The observed sudden sharp decrease of
potential corresponds to the adsorption of one mole hydrogen. At
the moment of the end of the hydrogenation the potential increases
sharply. Moreover a comparison of the velocity constants and of
the altitude of the potential of different catalysts is carried
out (Table 3). The following 2 phenomena were discovered at the
different catalysts. On catalysts unsaturated with hydrogen the
displacement of potential is essentially greater than on
saturated catalysts; that means that hydrogenation takes place
on a decrease in the potential which lasts till the end of the
hydrogenation of cyclopentadiene. The slowest stage in the
catalytic process was supposed to be the stage of the secondary
saturation. But this supposition did not prove true. On catalysts
not saturated up to the reciprocal hydrogen potential an induced

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Adsorption and Catalysis. Communication 3. Successive   SOV/62-59-7-4/38
Hydrogenation of Cyclopentadiene

final saturation takes place at the end of the hydrogenation
reaction. By means of the investigations on the adsorption of
the cyclopentene and of the cyclopentadiene and of the mixture
of both (Figs 5, 6, 7 and Tables 4, 5), a method of the complete
hydrogenation was developed allowing a study of the adsorption
of mixtures. It could be developed out of the fact that the
adsorption of the cyclopentene is generally greater than the
adsorption of the cyclopentadiene, whereas in mixtures the
opposite holds. The essential factor of the successive hydro-
genation is consequently this that the pentene is displaced from
the surface of the catalyst by the cyclopentadiene being more
strongly adsorbed out of the mixture according to the existing
adsorption properties of both substances in mixture. There are
7 figures, 5 tables, and 10 references, 8 of which are Soviet.

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the Academy of Sciences, USSR)

Card 3/4

Adsorption and Catalysis. Communication 3. Successive   SOV/62-59-7-4/38
Hydrogenation of Cyclopentadiene

SUBMITTED: August 22, 1957

Card 4/4

5 (4)

AUTHORS: Balandin, A. A., Freydlin, L. Kh.,   SOV/62-59-7-5/38
             Nikiforova, N. V.

TITLE: Kinetics of the Catalytic Reduction of Peroxides and Hydroper-
             oxides (Kinetika kataliticheskogo vosstanovleniya perekisey i
             gidroperekisey). Communication 3. Hydrogenation of 3-Hydro-
             peroxide-3-methyl-1-butine and of the Paranitrobenzoyl Peroxide
             (Soobshcheniye 3. Gidrirovaniye 3-gidroperekisi-3-metil-1-butina
             i perekisi paranitrobenzoila)

ABSTRACT: In this paper the successive hydrogenation of the groups $C \equiv C$,
             O-O, N=O, C=C was investigated by the catalytic reduction of the
             compounds (I) and (II) mentioned in the title. From the energy
             principles of the multiple theory (Ref 2) it follows that the
             reduction with the lowest energy barrier begins as the first
             reaction. The height of the energy barrier can be calculated
             from the binding energy between the atoms reacting in catalysis.
             In the reduction of (I) the groups O-O and $C \equiv C$ and the groups
             C=C, C-O and C-C being formed in the course of the reaction
Card 1/4   compete in this regard. The energy barriers of the individual

Kinetics of the Catalytic Reduction of Peroxides and   SOV/62-59-7-5/38
Hydroperoxides. Communication 3. Hydrogenation of 3-Hydroperoxide-3-methyl-1-
butine and of the Paranitrobenzoyl Peroxide

bonds calculated from the average binding energy of the reacting
atoms are:

O-O, $-E_1 = -14.2$ kcal/mol

C≡C, $-E_3 = -6.4$ "

C=C, $-E_2 = 2.9$ "

C-O, $-E = 17$ "

C-C, $-E = 48$ "

The first reduction thus begins on the O-O bond. The values -E
of (II) for the bond O-O, N=O or N-O are:

N-O, $-E_4 = -28.3$ kcal/mol | C=C$_{benz}$ $-E = 20$ kcal/mol

O-O, $-E_1 = -14.2$ " | C-C$_{aliph}$ $-E = 48$ "

The numeric values of the binding energies were taken from the
paper, reference 3. The sequences of the hydrogenation reactions
may be seen from the values -E. The experimental data obtained
gave the proof of the supposed sequence of the reduction of the
single binding groups in the compounds (I) and (II). A nickel

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Kinetics of the Catalytic Reduction of Peroxides and   SOV/62-59-7-5/38
Hydroperoxides. Communication 3. Hydrogenation of 3-Hydroperoxide-3-methyl-1-
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catalyst was used for the investigation. The kinetics and the
sequence of the hydrogenation of the bonds (Fig 1), the influence
of the temperature on the hydrogenation rate (Figs 2, 6), the
activating energy (Figs 3, 7) and the hydrogenation kinetics in
the presence of palladium, (Fig 4, a, b) were investigated. The
data of the hydrogenation kinetics of bifunctional peroxide
compounds on skeleton nickel are given in a table for comparison.
The sequence of the hydrogenation reaction depends also on the
kind of catalyst. On a platinum catalyst the acetylene bond is
hydrogenated first and   the 0-0 bond afterwards. A strict
selectivity is only to be noticed when hydrogenating the triple-
and double bond. There are 7 figures, 1 table , and 14 references,
8 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk
                SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the
                Academy of Sciences, USSR)

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Kinetics of the Catalytic Reduction of Peroxides and   SOV/62-59-7-5/38
Hydroperoxides. Communication 3. Hydrogenation of 3-Hydroperoxide-3-methyl-1-
butine and of the Paranitrobenzoyl Peroxide

SUBMITTED: October 26, 1957

Card 4/4

5 (4)

AUTHORS: Balandin, A. A., Karpeyskaya, Ye. I.,   SOV/62-59-8-4/42
Tolstopyatova, A. A.

TITLE: On the Catalytic Properties of Rhenium. Communication 1.
Rhenium as a Dehydrogenation Catalyst

ABSTRACT: On the basis of the structural conditions of the multiplet theory
it was to be expected that rhenium had a dehydrogenating effect
upon hydro-aromatic hydrocarbons. Platonov (Ref 13) reported
on such a dehydrogenation upon rhenium, but did not describe the
reaction conditions nor the preparation of the catalysts. In
the present paper the data cited by Platonov are checked and
investigations of the capability of dehydrogenation of Re on
hydrocarbons by means of different catalysts (powdery catalysts
and carrier catalysts) are carried out. The catalytic activity
of the catalysts with regard to cyclohexane was investigated.
It was shown that it is possible to dehydrogenate cumene as well
as to dehydrocyclize n-heptane on Re. In the experimental part
the preparation of 10 catalysts is described. (Catalysts 1 and 2
Card 1/3   according to Platonov's nitric acid method (Ref 4)).

On the Catalytic Properties of Rhenium.   SOV/62-59-8-4/42
Communication 1. Rhenium as a Dehydrogenation Catalyst

Catalysts 1-3 were prepared from ammonium perrhenate, catalysts
4, 5 were Re on aluminum (Re-contents 25 and 60.8%), 6: Re on
asbestos, 7: Re on silica gel, 8, 9: Re on activated coal,
10: Re on activated boneblack (Re percentages are given). The
initial materials were isopropyl alcohol, cyclohexane,
n-heptane, and cumene. The catalytic reaction rate was
determined from the amount of hydrogen separated out. The gas
analysis was done on a VTI unit. The results of the individual
reactions on the various catalysts are compiled in tables 1-8
and figures 1-4. It was found that for the dehydrogenation of
isopropyl alcohol on catalysts 1 and 2 an activation energy of
10.4 and 12.0 kcal/mol, respectively, is necessary, as was also
shown by Platonov (Ref 3). The dehydrogenation of cyclohexane
and -hexene did not succeed upon catalysts 1, 2, 3, 6, 7, while
the yield was low with 4 and 5. Cyclohexane is transformed into
cyclohexene, which is explained by the doublet mechanism
of these two catalysts with regard to the dehydrogenation of the
two substances. The carrier catalysts Re on activated coal proved
to be the most active ones. It was concluded from these results

Card 2/3   that the type of carrier plays an important part in catalytic

On the Catalytic Properties of Rhenium.   SOV/62-59-8-4/42
Communication 1. Rhenium as a Dehydrogenation Catalyst

reactions. The characteristic of this part is the ratio of the
difference in the atomic distances of metal atoms and carrier
atoms. N-heptane on catalyst 9 resulted in 14.1% toluene, while
cumene on catalyst 9 produced α-methylstyrene and, partly,
its polymerizate. There are 6 figures, 8 tables, and
15 references, 11 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii
               nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy,
               of the Academy of Sciences, USSR)

SUBMITTED: November 5, 1957

Card 3/3

5(4)

AUTHORS: Bogdanova, O. K., Balandin, A. A.,   SOV/62-59-8-5/42
            Shcheglova, A. P.

TITLE: Effect of the Structure of Alcohol Molecules on the Kinetics
            of Dehydrogenation. Communication 4: Catalytic Dehydrogena -
            tion of Benzyl Alcohol

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
            1959, Nr 8, pp 1372-1377 (USSR)

ABSTRACT: A flow system described in (Ref 1) was used for the investi-
            gation of the dehydrogenation kinetics. The constancy of
            catalytic activity was checked in the course of the experiment
            by means of benzyl alcohol and a mixture of benzyl alcohol
            and its reaction products. The benzaldehyde contents of the
            catalyst were determined by the method described in reference 4.
            The reaction rate was determined from the amount of hydrogen
            separated out per time unit. The two determinations were in
            good agreement. The reaction was investigated at 4 different
            rates of passage (1.02, 1.23, 1.33, and 1.8 ml in 5 min). The
            benzaldehyde yield increased from 8.2% to the predetermined
            yield of 61%. The results are compiled in table 1. The cal-
Card 1/3   culated degree of dehydrogenation and benzaldehyde yield are

Effect of the Structure of Alcohol Molecules on the   SOV/62-59-8-5/42
Kinetics of Dehydrogenation. Communication 4: Catalytic
Dehydrogenation of Benzyl Alcohol

in agreement. In order to investigate the mixture mentioned
above the adsorption coefficient of benzaldehyde was deter-
mined during the reaction. (Results in Table 2). It is stated ·
that the reaction is slowed down when benzaldehyde is added.
A temperature increase results in a reduction of the adsorp-
tion coefficient. A change in the initial mixture of benzal-
dehyde and benzalcohol does not effect the adsorption coef-
ficient. With high passage rates it is reduced, but becomes
constant with particularly high rates (Table 4). According to
formula (1) Δ = -RT ln.z_2 (z_2 adsorption coefficient of benzal-
dehyde) the heat content and entropy in the adsorption dis-
placement of the alcohol by the aldehyde were determined. When
the dehydrogenation temperature is increased the aldehyde yield
can be increased greatly. This may be of practical value in
the preparation of benzaldehyde. There are 4 figures, 4 tables,
and 5 references, 4 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk
                SSSR) Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy
Card 2/3   of Sciences, USSR)

Effect of the Structure of Alcohol Molecules on the   SOV/62-59-8-5/42
Kinetics of Dehydrogenation. Communication 4: Catalytic
Dehydrogenation of Benzyl Alcohol

SUBMITTED: November 20, 1957

Card 3/3

5 (3)

AUTHORS: Polkovnikov, B. D., Freydlin, L. Kh.,   SOV/62-59-8-27/42
              Balandin, A. A.

TITLE: Selective Hydrogenation of the Dinitrile of Adipic Acid on a
              Cobaltboride Catalyst

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
              1959, Nr 8, pp 1488-1490 (USSR)

ABSTRACT: The hydrogenation of the dinitrile of adipic acid usually proceeded
              very badly on the catalysts used so far on account of the
              formation of by-products (secondary amines) inhibiting the
              reaction (Refs 1-3). The authors therefore in the present paper
              used the catalyst Co_2B for the activation of the reaction
              mentioned above and investigated its effectiveness. The catalytic
              properties of Co_2B had so far not been described in literature.
              The catalyst was prepared according to the method (Ref 5) used
              for nickel borides. The hydrogenation was carried out in a
              rotary autoclave. The results of the investigation are collected
              in the table and figures. The experiments were made in the
              presence of ammonia as well as without ammonia. The high
              hexamethylenediamine yields in the absence of ammonia (71-83.6%)

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Selective Hydrogenation of the Dinitrile of Adipic   SOV/62-59-8-27/42
Acid on a Cobaltboride Catalyst

were even increased to 89% when ammonia was present. The use of
larger amounts of ammonia did, however, not increase the yield
above that level. The formation of secondary amines, which is
considerably accelerated on a nickel skeleton catalyst at
$80-100°$, has no effect as yet upon the diamine yield on Co_2B
at $125°$. Furthermore the effect of the amount of catalyst used
upon the reaction direction was investigated. It was found that
a change in this amount has no effect upon the yield so that a
continuously operating apparatus may be used for the reaction
as well. The investigation results suggest that on Co_2B the
reaction is selective and takes place according to the following
equation only, while there is hardly any formation of by-products:

$$NC-(CH_2)_4-CN \xrightarrow{+H_2} NH_2-(CH_2)_5-CH=NH \xrightarrow{+H_2} NH_2-(CH_2)_6-NH_2 \quad (1).$$

There are 1 figure, 1 table, and 7 references, 4 of which are
Soviet.

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Selective Hydrogenation of the Dinitrile of Adipic   SOV/62-59-8-27/42
Acid on a Cobaltboride Catalyst

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk
               SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy
               of the Academy of Sciences, USSR)

SUBMITTED: February 7, 1959

Card 3/3

5 (2)

AUTHORS: Balandin, A. A., Turova-Polyak, M. B.,   SOV/62-59-8-33/42
             Levi, G. I., Kheyfits, L. A.

TITLE: On the Formation of Elementary Phosphorus Under the Effect of
             Hydrogen and Vapors of Organic Substances on a Phosphoric Acid
             Catalyst on Activated Coal

ABSTRACT: In this short communication the authors report on the conditions
             and causes of elementary phosphorus forming during work with the
             above mentioned phosphoric acid catalyst. When hydrogen and
             vapors of organic substances pass over the catalyst the formation
             begins at 400° and, in the case of nitrogen, at 600°. Oxygen
             traces in the vapors prevent phosphorus formation. It is supposed
             that the phosphorus reduction is effected by the especially active
             surface atoms of the activated coal and the hydrogen atoms. There
             is 1 Soviet reference.

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On the Formation of Elementary Phosphorus Under the   SOV/62-59-8-33/42
Effect of Hydrogen and Vapors of Organic Substances on a Phosphoric Acid
Catalyst on Activated Coal

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova
                (Moscow State University imeni M. V. Lomonosov). Institut
                organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR
                (Institute of Organic Chemistry imeni N. D. Zelinskiy, Academy
                of Sciences, USSR)

SUBMITTED: February 19, 1959

Card 2/2

5(2)   SOV/62-59-9-4/40
AUTHORS: Balandin, A. A., Karpeyskaya, Ye. I., Tolstopyatova, A. A.

TITLE: On the Catalytic Properties of Rhenium. Report 2. Dehydrogena-
                tion of Cyclohexane

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
                1959, Nr 9, pp 1529-1535 (USSR)

ABSTRACT: Cyclohexane is dehydrogenized on activated carbon by rhenium
                (Ref 1). In the present paper the authors subjected the mode of
                operation of the catalyst in the dehydrogenation process to
                closer investigations. They determined the effect of the rhenium
                content in the catalyst on the activating rate and energy of
                the above-mentioned reaction. The reaction process in the pre-
                sence of benzene and hydrogen was also investigated; therefrom
                it was possible to determine the relative adsorption coefficient
                of the reaction products. The following catalysts were used:
                catalyst Nr 9 of reference 1 and catalysts Nr 11 (Re 4.86%),
                Nr 12 (Re 9.45%), Nr 13 (Re 16.6%), Nr 14 (Re 38.4%), Nr 15
                (Re 42.5%). The determination methods were the same as in previ-
                ous investigations (Refs 1,2). Hydrogen was added with a gaso-
Card 1/3   meter (system Patrikeyev, reference 4). The influence of the

SOV/62-59-9-4/40

On the Catalytic Properties of Rhenium. Report 2. Dehydrogenation of Cyclo-hexane

rhenium content in the catalysts appeared in the following way:
(analysis results of the reaction products in tables 1, 2 and
on figures 1, 2). Pure, activated carbon had the least activity
and the reaction proceeded at very high temperatures only. The
reaction process was observed to proceed according to different
mechanisms on pure carbon and on Re-catalysts. The value

$\dfrac{\varepsilon}{lg\, k_o}$ was a maximum for catalyst Nr 9 (best catalyst) (Re con-

tent 29.6%). The adsorption coefficient "z" was determined for
benzene and hydrogen on catalyst Nr 9 (Tables 4,6); z was de-

termined according to formula $z = \dfrac{m_o/m-1}{100/P-1}$. The adsorption co-

efficient is temperature independent. The dehydrogenation reac-
tion on the Re-catalyst is a reaction of the order of zero. The
activation energy was from 12.8 (Nr 9) to 20.3 kcal. There are
2 figures, 6 tables, and 6 references, 4 of which are Soviet.

Card 2/3

SOV/62-59-9-4/40

On the Catalytic Properties of Rhenium. Report 2. Dehydrogenation of Cyclohexane

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: December 30, 1957

Card 3/3

5 (3)

AUTHORS: Freydlin, L. Kh., Balandin, A. A.,   SOV/62-59-9-20/40
                 Zhukova, I. F., Yakovlev, I. P.

TITLE: Investigation of the Selective Effect of Catalysts. Communica-
                 tion 3. Hydration of Isoprene on a Skeleton Nickel Catalyst

ABSTRACT: The hydration of isoprene on a skeleton nickel catalyst was in-
                 vestigated without (Fig 1) and with the addition of pyridine
                 (Fig 2), and under pressure. The step-by-step hydration of the
                 isoprene was established by determining the diene content in the
                 catalyst before and after the consumption of 1 mol of hydrogen.
                 After consumption of 1 mol of H no diene could be detected in
                 the catalyst, which confirms the stepwise hydration. The diene
                 was determined according to B. N. Afanas'yev (Ref 6) or A. Baeyer
                 (Ref 7). The authors found that the step-by-step hydration oc-
                 curs as well with as without pyridine and that at experiments
                 with small quantities of pyridine the reaction proceeds only to
                 the formation of monoolefines. The influence of the quantity
                 pyridine/catalyst surface and the influence isoprene/catalyst
Card 1/2   surface (Tables 3,4) was investigated concerning Ni + pyridine

Investigation of the Selective Effect of Catalysts.   SOV/62-59-9-20/40
Communication 3. Hydration of Isoprene on a Skeleton
Nickel Catalyst

and found that an excess of pyridine hinders the isoprene hy-
dration. The analysis of the reaction products of the Ni + py-
ridine experiment was carried out with the Raman spectrum. The
two isomer substances 2-methylbutane-1 and 2-methylbutane-2
were present in the catalyzate. At variations of the pressure
the selective effect of pyridine remained up to a pressure of
80 atm. Quinoline has the same effect as pyridine. There are
2 figures, 5 tables, and 9 references, 6 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk
SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of
the Academy of Sciences, USSR)

SUBMITTED: December 20, 1957

Card 2/2

5(3)   SOV/79-29-5-2/75

AUTHORS: Borunova, N. V., Balandin, A. A., Freydlin, L. Kh.

TITLE: On the Selectivity of the Action of Applied Nickel-Aluminum
              Oxide Catalysts (O selektivnosti deystviya nanesennykh nikel'-
              glinozemnykh katalizatorov)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 5,
              pp 1409 - 1412 (USSR)

ABSTRACT: It was found previously (Ref 1) that it is possible to obtain a nickel-
              aluminum oxide catalyst by the reduction of a mixture of nickel
              monoxide and aluminum oxide which was formed by common precipi-
              tation and treatment with water vapors under pressure. In the
              presence of such a catalyst the double bonds C-C and C-O are
              hydrogenated, but not the aromatic bonds. In the present paper
              the authors investigated the selectivity of such catalysts which
              were obtained from nickel monoxide applied on aluminum oxide and
              treated with water vapor or carbon dioxide. The catalysts
              applied prepared by treatment with water vapors were found to
              hydrogenate selectively the ethylene bond of octene-3 or styrene
              in the presence of an aromatic bond (Table 1). It was shown

Card 1/2   to be possible to regulate the activity of the catalysts obtained

On the Selectivity of the Action of Applied Nickel-   SOV/79-29-5-2/75
Aluminum Oxide Catalysts

by treating the mixture of nickel monoxide and aluminum oxide
with carbon dioxide under pressure and to give them a specific
efficiency (Table 2). The inactivation of the catalyst by
treatment with carbon dioxide was proved to be reversible in
contrast with the steam treatment. There are 2 tables and 4
Soviet references.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute
of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: May 6, 1958

Card 2/2

5(3)

SOV/79-29-7-23/83

AUTHORS: Bogdanova,O. K., Balandin, A. A., Shcheglova, A. P.

TITLE: Preparation of Butadiene by Catalytic Dehydrogenation of Butane -
             butylene Mixtures in the Presence of Steam (Poluchoniye
             butadiyena katalitichoskoy degidrogenizatsiyey butan-
             butilenevykh smesoy v prisutstvii parov vody.)

ABSTRACT: One of the most important methods of synthesizing butadiene is
             the catalytic dehydrogenation of butylene into butadiene.
             Butylene may be obtained from cracking gases and in petroleum
             pyrolysis or by dehydrogenolysis of butane. In this connection,
             however, butylene is obtained in a mixture with butane so that
             this mixture must be fractionated in the presence of a third
             component. Industrial preparation of butadiene should practi-
             cally be carried out without separating butylene from butane in
             the above mixture. Earlier (Ref 1) the authors investigated the
             dehydrogenolysis of butane-butylene mixtures over a chromium
             catalyst at reduced pressure and obtained good yields in
             butadiene. Some patents (Refs 2-4) offered only low yields.
             The authors of this paper tried to investigate the effect of
Card 1/2   steam on the dehydrogenolysis of butane-butylene mixtures,

Preparation of Butadiene by Catalytic Dehydrogenation of SOV/79-29-7-23/83
Butane - butylene Mixtures in the Presence of Steam

viz over a catalyst suited for dehydrogenolysis carried out in
the presence of steam since the latter is the most convenient
diluent. Steam is known to favor, in the presence of some
catalysts and at increased temperatures, the cracking process
of hydrocarbons. Dehydrogenolysis of the above mixtures may take
place in the presence of steam over an oxide catalyst for the
dehydrogenolysis of butylene. Under these conditions the
butadiene yields were 40% computed for the butylene passing
through, and 75-80% computed for the reacted mixture. It is
not necessary to regenerate the catalyst also after longer
usage. The chromium-aluminum catalyst retards the dehydrogenolysis
of butane into butylene in the presence of steam and converts
the latter partially into decomposition products. Without diluent
at 635° the butadiene yields over the same catalyst were 11.6%,
computed for the mixture passed through, in this case the
catalyst had to be regenerated several times. There are 4
figures, 5 tables, and 10 references, 6 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of
Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: April 15, 1958

Card 2/2

5(4)

AUTHORS: Balandin, A. A., Spitsyn, Vikt. I.,   SOV/76-33-3-39/41
               Barsova, L. I., Duzhenkov, V. I.

TITLE: Radiation Method for the Production of Platinum Catalysts
               (Radiatsionnyy metod polucheniya platinovogo katalizatora)

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 3, pp 736-737
               (USSR)

ABSTRACT: Though various papers have already been published on the
               effect exercised by ionizing radiations on catalytic re-
               actions (Refs 1,2), the action of radiations has not yet been
               employed in the production of the catalyst. In this case the
               authors investigated the separation of metallic platinum
               from some of its complex compounds by the action of a flux
               of fast electrons; further, they studied the structure and
               catalytic properties of the precipitates obtained. A radiation
               source was applied as a linear electron accelerator with
               1.5 mev (Ref 3). The capacity of each dose was determined by
               the ferroussulphate method; it amounted to $1.5.10^{18}$ ev/cm^3
               per second. It was shown by radiation of saturated solutions
               of $Na_2[Pt(OH)_6]$ in 0.5-3 n NaOH that in doses above

Card 1/3

Radiation Method for the Production of Platinum   SOV/76-33-3-39/41
Catalysts

5.10^{21} ev/cm^3 a yellow precipitate is obtained which assumes
a metallic-gray coloration by the action of radiation.
N. A. Shishakov made X-ray analyses which indicated that
crystalline platinum and the partially unreduced compounds
of Pt^{4+} are present in the precipitate. The most interesting
results were offered by saturated solutions of $Na_2[Pt(OH)_xCl_{6-x}]$
in 2 n NaOH at doses of 2.10^{21} ev/cm^3. In this case a black
platinum precipitate was obtained, the particle size of which
depended on the concentration of the solution and the time
of irradiation. The reduction to the metal is perfect in this
case. The platinum precipitates obtained were checked with
respect to their catalytic activity in the reduction of the
low-temperature hydrogenation of cyclohexane and were com-
pared with platinum catalysts produced by Loev's (Lev's)
method. During the first days after radiolysis the afore-
said catalysts were more active by fifteen to twenty times,
later this activity decreased, yet remained above that of
the catalysts according to Loev. The experiments will be
Card 2/3   continued. There are 4 references, 2 of which are Soviet.

Radiation Method for the Production of Platinum   SOV/76-33-3-39/41
Catalysts

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova,
                Akademiya nauk SSSR, Institut fizicheskoy khimii (Moscow
                State University imeni M. V. Lomonosov, Academy of Sciences
                USSR, Institute of Physical Chemistry)

SUBMITTED: December 22, 1958

Card 3/3

5(4)   SOV/76-33-4-12/32

AUTHORS: Kiperman, S. L.,   Balandin, A. A.

TITLE: The Bond Energy of the Surface of Metallic Catalysts With
              Hydrogen and Deuterium (Energiya svyazi poverkhnosti metalli-
              cheskikh katalizatorov s vodorodom i deyteriyem)

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 4, pp 828-834
              (USSR)

ABSTRACT: In a previous paper (Ref 8) a report was given on the applica-
              tion possibility of a variant of the kinetic method of determin-
              ing the formation energy (FE) of nickel catalysts with elements
              of organic compounds. In the present case the amount of (FE)
              of different metallic catalysts (Ni, Fe, Pt and Pd) with hydro-
              gen (I) and deuterium (II) was determined. The reaction of the
              para-ortho-conversion of (I), of the ortho-para-conversion
              of (II) and of the isotopic exchange of (I) with (II) was used
              for the computation of (FE) from the kinetic data. The com-
              putations are made according to the derived equations (4)-(7),
              (9), (10), (12) and (13) as well as according to the correspond-
              ing data from publications. The values of (FE) obtained with
              (I) and (II) are tabulated. (Table). The (FE)-values for dif-
              ferent metals are rather similar; however, it is pointed out
Card 1/2   that the reaction mechanism on some catalysts is determined by

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The Bond Energy of the Surface of Metallic Catalysts With Hydrogen and Deuterium

adsorption and on others by desorption so that this fact may explain a difference. On the basis of the similar (PE)-values it is assumed that the reaction on the various metal surfaces takes place mainly on the active spots which show optimum (PE)-values. Since in the determination of (PE) according to heat absorption on the one hand, only the active spots at which adsorption takes place are taken into account, and on the other hand, equation (16) assumes a complete destruction of the bonds whereas in the case of the kinetic method (on the basis of the multiplet theory of catalysis) only a deformation of the bonds is assumed, the (PE)-values obtained according to the kinetic method and those obtained from the values of adsorption heat differ from each other. It is said that special investigations must be carried out on the applicability of the Pauling rule for the above determinations. There are 1 table and 33 references, 17 of which are Soviet.

ASSOCIATION: Akademiya nauk SSSR, Institut organicheskoy khimii im. N. D. Zelinskogo (Academy of Sciences of the USSR, Institute of Organic Chemistry imeni N. D. Zelinskiy)

SUBMITTED: September 18, 1957

Card 2/2

5(4)   SOV/76-33-9-26/37

AUTHORS: Kiperman, S. L., Balandin, A. A.

TITLE: The Bond Energies of the Surface of Metallic Catalysts
                With Carbon

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 9,
                pp 2045 - 2052 (USSR)

ABSTRACT: The applicability of a variation of the kinetic method
                (Ref 3) used for the determination of the bond energies
                of the surface of nickel catalysts with elements of organic
                compounds was indicated in previous articles (Refs 1,2).
                Further, the bond energy (BE) of hydrogen (I) with metallic
                catalysts (C) was calculated. This method is used here for
                a determination of the (BE) of the surface of metallic (C)
                with carbon (II). It was based on the amount of (BE) with
                light and heavy (I), which had been obtained by reactions
                of para- and ortho-conversion and the activation energy of
                the isotopic exchange, the hydrogenation and hydrogenolysis
                of organic compounds in the presence of these (C). The forma-
                tion of duplet complexes between the initial substance (IS)
Card 1/3   and the (C) is considered to be a slowly proceeding inter-

The Bond Energies of the Surface of Metallic Catalysts   SOV/76-33-9-26/37
With Carbon

mediate stage which is termed adsorption stage (AS). On the
basis of the multiplet theory of catalysis the (AS) is cha-
racterized by the height of the energy barrier E, which depends
on the adsorption heat of the (IS) on the catalytically active
parts of the (C)-surface. The authors investigated the follow-
ing reactions and calculated the (BE) of (II) with the sur-
faces of Ni, Fe, Pt, and Pd catalysts (Table):

$C_2H_6+H_2 = 2 CH_4$ (1), $CH_4+D_2 = CH_3D+HD$ (2), $C_2H_4+H_2=C_2H_6$ (8),

$C_2H_4+D_2=C_2H_3D+HD$ (9), $C_2H_2+H_2=C_2H_4$ (14), $CH_3C=CH+H_2=CH_3CH=$

$=CH_2$ (15), $C_6H_6+D_2=C_6H_5D+HD$ (21). The resultant (BE) are mean
values of the reactive region of the (C)-surface. A multiple
bond of (II) increases the strength of the (II)-bond with re-
spect to the (C)-surface. The formation of a tricyclic or
aromatic ring in addition to a simple or double bond, for
example, yields a (II)-(C) bond that is stronger than that of
(II). With a slight variation in the activity of the (C),

Card 2/3   as well as with a transition from the one metal to the other,

The Bond Energies of the Surface of Metallic Catalysts SOV/76-33-9-26/37
With Carbon

> also the corresponding (BE) varies to a relatively small
> extent. This indicates that the reaction of organic compounds
> with (II) on the (C)-surface apparently proceeds at the
> points of maximum (BE). In conclusion, the scientist V. N.
> Kondrat'yev is mentioned. There are 1 table and 24 refer-
> ences, 9 of which are Soviet.

ASSOCIATION: Akademiya nauk SSSR, Institut organicheskoy khimii im. N. D.
Zelinskogo (Academy of Sciences of the USSR, Institute of
Organic Chemistry imeni N. D. Zelinskiy)

SUBMITTED: March 6, 1958

Card 3/3

5. 1190
5(4)

66860
SOV/76-33-11-15/47

AUTHORS: Balandin, A. A., Karpeyskaya, Ye. I., Tolstopyatova, A. A.

TITLE: Principle of the Structural Congruence and the Catalytic
             Properties of Rhenium

ABSTRACT: Starting from the multiplet theory one may assume that rhenium
             may act as a dehydrogenation catalyst (as Pt, Pd, Ir, Rh, Co, and
             Ni with the structural lattice A 1 and Os, Ru, Co, and Ni with
             the lattice A 3), as it has an A 3 lattice and an atomic radius
             of 1.37 Å. M. S. Platonov (Ref 2) pointed out at the Conference
             on Catalysis of 1940 that rhenium cyclohexane can dehydrogenate
             at 300-350°, but he did not present any experimental data. In
             the present case an active rhenium catalyst was obtained by
             preparing from Re_2O_7 and dioxane a $Re_2O_7 \cdot xC_4H_8O_2$ precipitate,
             which was dissolved in methanol. In one case the solution was
             deposited on active carbon (birch charcoal) and heated for
             several hours to 500° in a hydrogen current, in the other case
             the methanol solution was deposited on asbestos and reduced.
Card 1/2   Three series of experiments on the dehydrogenation of cyclic

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SOV/76-33-11-15/47
Principle of the Structural Congruence and the Catalytic Properties of Rhenium

hydrocarbons were carried out in a continuously working apparatus, and the gas formed was analyzed in the apparatus VTI. The dehydrogenation of the cyclohexane occurred at 250-340°. It was thus shown that the Re/C catalyst (Table 1) is more effective than the Re/asbestos catalyst (Table 2), but the activation energy remains the same (7.8 kcal/mol) and the composition of the gas is almost independent of the temperature. The structure important for the catalyst depends not only on the catalyst carrier, but also on the method of preparation, since one catalyst was inactive. The latter had been produced by applying rhenium acid to asbestos. The dehydrogenation of methyl cyclohexane occurred on the Re/C catalyst at 270-320°. It showed (Table 3) that the methane content of the gas is temperature-dependent. During the dehydrogenation of ethyl cyclohexane on the Re/C catalyst at 286-388° (Table 4), it was also found that the gas composition is temperature-dependent. There are 1 figure, 4 tables, and 5 Soviet references.

ASSOCIATION: Akademiya nauk SSSR, Institut organicheskoy khimii im. N. D. Zelinskogo (Academy of Sciences, USSR, Institute of Organic Chemistry imeni N. D. Zelinskiy)

Card 2/2

5.3200
5(4)

66861
SOV/76-33-11-16/47

AUTHORS: Balandin, A. A.; Bogdanova, O. K., Shcheglova, A. P.

TITLE: Influence of the Structure of Alcohol Molecules on the Kinetics
               of Their Dehydrogenation

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 11, pp 2476-2479
               (USSR)

ABSTRACT: The dehydrogenation kinetics of the following alcohols was in-
               vestigated on oxide catalysts: ethanol, n-propanol, n-butanol,
               allyl alcohol, isoamyl alcohol, isopropanol, benzyl alcohol,
               and β-phenyl ethyl alcohol. The experiments were carried out
               by means of a device and method earlier described (Ref 1). The
               reaction constants of alcohol dehydrogenation obtained (Table 1)
               increase from allyl alcohol to benzyl alcohol. The values of the
               free energy of displacement from the active catalyst surface
               and of the change ΔH are listed (Table 2). Moreover, the
               authors explain the effect of the structure on the activation
               energy (Ref 3) and the variation in the heat of adsorption dis-
               placement and entropy. In addition, they found that the structure
               has some effect. Accordingly, an extension of the hydrocarbon
Card 1/2   chain in the primary alcohol leads to a decrease of the acti-

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Influence of the Structure of Alcohol Molecules on the Kinetics of Their De-
hydrogenation

vation energy. Replacement of the hydrogen by a phenyl group in
β-position increases the activation energy by 0.3 kcal. However,
if the phenyl group is found on the same carbon atom as the
hydroxyl group, the activation energy decreases. A parallelism
was observed between the variations in entropy (ΔS) and
enthalpy (ΔH) (Fig 2) in adsorption displacement of the alcohol
molecules by corresponding aldehydes or ketones from the catalyti-
cally active centers which occurs during alcohol dehydrogenation.
This parallelism was observed for the first time in adsorption
processes. A logarithmic dependence between activation energy
and reaction constant was found. There are 2 figures, 2 tables,
and 10 Soviet references.

ASSOCIATION: Akademiya nauk SSSR, Institut organicheskoy khimii im. N. D. Ze-
linskogo (Academy of Sciences, USSR, Institute of Organic
Chemistry imeni N. D. Zelinskiy)

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5.1190

3(4)

66862

SOV/76-33-11-17/47

AUTHORS: Balandin, A. A., Klabunovskiy, Ye. I.

TITLE: Stereochemical Investigation of the Mechanism of Catalysis

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 11, pp 2480-2484
(USSR)

ABSTRACT: The catalytic hydrogenation of several trypticene derivatives
was carried out with nickel, as these have a complicated
steric configuration and therefore they do not adjust them-
selves easily to the catalyst surface, which renders them
suitable for this study (from the viewpoint of the multiplet
theory). The application of stereochemical principles together
with those of the multiplet theory permits the recording of
models of intermediary active complexes (Figs 2,3). It was
shown that, despite complicated configuration of the original
substances which prevent the laying on a plane catalyst sur-
face, hydrogenation occurs already at 45° and 1 atm. Therefore
the catalysis occurs on the elevations of the catalyst, besides
hollows where the protruding molecule parts deposit in the
hollows. The models of the compounds investigated permit
evaluation of the depth of these hollows with a minimum of

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SOV/76-33-11-17/47

Stereochemical Investigation of the Mechanism of Catalysis

3.17 Å and a maximum width of 4.8 Å. Thus, a method is obtained for the determination of the microrelief of the catalyst surface. There are 3 figures and 9 references, 6 of which are Soviet.

ASSOCIATION: Akademiya nauk SSSR, Institut organicheskoy khimii im. N. D. Zelinskogo (Academy of Sciences, USSR, Institute of Organic Chemistry imeni N. D. Zelinskiy)

Card 2/2

5. 2600(A)
5. 3200

66863

~~5(4)~~
SOV/76-33-11-18/47

AUTHORS: Balandin, A. A., Freydlin, L. Kh., Nikiforova, N. V.

TITLE: The Kinetics of Selective Catalytic Hydrogenation[1] of Bifunc-
                 tional Peroxides and Hydrogen Peroxides on Nickel. Prediction
                 of Reactions on the Basis of the Multiplet Theory

ABSTRACT: Due to the explanations of Kottrell (Ref 1) on the binding
                 energy, it was recently possible to determine the value of the
                 energy of the peroxide bond -O-O-. Now it became possible to
                 calculate the relative ease of hydrogenolysis of this bond on
                 the nickel catalyst with the aid of energy equations of the
                 multiplet theory (if the quantities required are known). The
                 calculation showed that the height of the energy barrier, which
                 determines the reaction rate is: $-E'' = -14.2$ kcal/mol (Table).
                 This table also contains the values of E for the hydrogenation
                 of various bonds on nickel, which were obtained with the aid of
                 equations of the multiplet theory. The equations (2) express the
                 formation energy E' and the decomposition energy E'' of a multi-
Card 1/2   plet complex M as a function of the binding energy Q. The

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The Kinetics of Selective Catalytic Hydrogenation of Bifunctional Peroxides
and Hydrogen Peroxides on Nickel. Prediction of Reactions on the Basis of the
Multiplet Theory

        multiplet theory predicts (Table, Equation (2)) that: 1) the
peroxide compounds are easily hydrogenated on nickel; 2) the
activation energy of these reactions is low; 3) the molecule
structure influences the hydrogenation rate; 4) polyfunctional
peroxides must follow a certain order of reaction in hydro-
genation on nickel (Table); 5) this order may change with other
catalysts. To check these predictions the authors experimentally
tested the hydrogenation of isopropyl benzene hydrogen peroxide,
ethyl phenyl isopropyl peroxide, tetralin hydrogen peroxide,
benzoyl peroxide, tert-butyl-perbenzoate, di-tert-butyl peroxide,
cyclohexene hydrogen peroxides, 3-hydrogen peroxides of 3-methyl-
1-butine and the peroxide of n-nitrobenzene. They further de-
termined the activation energy. All of the above-mentioned pre-
dictions made according to the multiplet theory were confirmed
by experimental data. There are 1 table and 5 Soviet references.

ASSOCIATION: Akademiya nauk SSSR, Institut organicheskoy khimii im. N. D. Ze-
               linskogo (Academy of Sciences, USSR, Institute of Organic
               Chemistry imeni N. D. Zelinskiy)

Card 2/2

5(3)   SOV/2o-124-3-3o/67
AUTHORS: Freydlin, L. Kh.,   Balandin, A. A., Academician, Zhukova, I.P.

TITLE: The Selective Hydrogenation of the Acetylene Bond in Butine-
             2-Diol-1,4 Into the Ethylene Bond on a Nickel Catalyst
             (Selektivnoye gidrirovaniye atsetilenovoy svyazi butin-2-
             diola-1,4 v etilenovuyu na nikelevom katalisatore)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 3, pp 598-601
             (USSR)

ABSTRACT: It is a well-known fact that, in the presence of pyridine
             (or quinoline), acetylene hydrocarbons are selectively hydro-
             genated into ethylene hydrocarbons on a skeletal nickel cata-
             lyst. Two experiments were carried out: (1) at normal pres-
             sure, 20°C, and strong shaking; (2) at increased pressure, in
             a rotating autoclave. Ethanol, methanol, dioxane, and di-
             methyl formamide were used as solvents. In ethanol or methanol
             only, butinediol is quickly hydrogenated into butanediol.
             However, the hydrogen absorption curve points to a gradual
             hydrogenation. In dioxane the reaction occurs more slowly. After
             the addition of pyridine, the reaction starts to become
Card 1/2   selective, the affiliation of the second hydrogen mol is

SOV/20-124-3-30/67

The Selective Hydrogenation of the Acetylene Bond in Butine-2-Diol-1,4
Into the Ethylene Bond on a Nickel Catalyst

significantly inhibited. At a higher pyridine concentration,
the reaction stops after the attachment of the first hydrogen
nol, hydrogenation does not go beyond the butenediol. In
pure pyridine, the selective reaction occurs slowly. It can
be accelerated by increased hydrogen pressure. The resulting
product was distilled in the vacuum and identified as butene-
diol. There are 2 figures, 1 table, and 5 references, 2 of
which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii
nauk SSSR
(Institute of Organic Chemistry imeni N. D. Zelinskiy of the
Academy of Sciences, USSR)

SUBMITTED: September 2, 1958

Card 2/2

5(3)   SOV/20-127-2-25/70
AUTHORS: Agronomov, A. Ye., Balandin, A. A., Academician, Mardashev, Yu.S.

TITLE: Comparison of the Kinetic Relative Adsorption Coefficients
                With Those Determined According to the BET Equation

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 2, pp 325-328
                (USSR)

ABSTRACT: The BET equation of the polymolecular adsorption which takes
                into account the interactions between adsorbent and adsorbed
                substance in the first layer and is related to the entire
                surface was derived in reference 1 (1938) (1). Its graphic
                solution makes the determination of the adsorption coefficient
                (AC) o possible. The second author in 1942 (Ref 2) derived an
                equation of the kinetics of the monomolecular reaction in a
                discharge system. A calculation method of the relative
                adsorption coefficient from kinetic data is given as well.
                This method made the determination of the value of these
                coefficients on the catalytically active centres of the
                surface possible. The equation (2) (identical with the equation
                (52) in reference 5) may be used for the determination of the
                relative adsorption coefficients from kinetic data.It was
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Coefficients With Those Determined According to the BET Equation

interesting to carry out the comparison given in the title.
The absolute AC differ according to reference 7 by two orders
of magnitude. The authors used the dehydrogenation reaction
of cyclohexane on Ni-catalysts (the latter on carriers). The
BET-AC were graphically determined from the equation (1).
The straight lines for the catalysts Nr 1 and 2 (Table 1) are
given in figure 1 as an example (5 catalysts were used and
their method of production is described here). AC according to
BET (c_{BET}) for benzene and cyclohexane were computed from the

tangent of the angle of gradient of this straight line; their
relation could be called the relative AC-BET (z_{BET})(Table 1 ,

columns 1-3). The kinetic relative AC were determined from the
equation (2). The reaction mentioned was carried out according
to the method of reference 10. The catalyst was used in a certain
quantity (volume V) so that the transformation did not exceed
30%. The equation (2) was transformed into (3) in the
experiments with pure cyclohexane. Furthermore, the experiment
was carried out with a mixture (with benzene) at the same

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temperature, then again with pure cyclohexane. This experiment
confirmed the observation of reference 11 that the activation
energy is not changed up to a mixture containing 10% benzene
(for the catalyst Nr 3). The two series of the values
(AC according to adsorption-, kinetic data respectively) are
very adjacent in the columns 3 and 4 of table 1. Thus, the
BET equation may be used in the case of the cyclohexane
dehydrogenation (Fig 1). The general equation of the kinetics
of the monomolecular reactions (Ref 4) holds as well in the
investigated region of the mixture composition, as it follows
from the constancy of z (Table 2). The relative AC of the
catalytic active centers turn out to be practically equal to
the relative AC of the entire surface. The fact that z_k and

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z_{BET} are equal is assumed to confirm the second author's
statement (Ref 12) that the places with a mean adsorption
intensity are catalytically active. There are 1 figure,
2 tables, and 12 references, 11 of which are Soviet.

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5(2,3)

AUTHORS: Balandin, A.A., Academician,   SOV/20-127-3-21/71
            Klabunovskiy, Ye.I., Petrov, Yu.I.

TITLE.   Configuration Interrelations in Stereospecific Catalysis

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 3,
            pp 557 - 560 (USSR)

ABSTRACT: The multiplet theory of catalysis shows the existence of
            a certain structural homology between the reacting molecule
            and the fine structure of the catalyst surface. These
            relations were investigated by several examples of the
            heterogeneous catalysis (Refs 1-3). Henceforth they have
            to be investigated in the field of asymmetric micro-
            heterogeneous catalysis, since the principles of the
            structural and energy correspondence of the multiplet
            theory was also applied to fermentative catalysis (Refs 4-6).
            The effectivity of the stereospecific catalysis depends on
            the degree of the structural correspondence. Therefore it
            is of interest to enlarge the knowledge about reactions
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(ferment samples). Skita catalyst (colloidal platinum or
palladium with gum arabic as protective colloid) was chosen
as such (Ref 7). These catalysts were produced according
to reference 9 which was altered according to reference 10.
Phenyl- and α-naphthyl- glyoxylic acids were chosen as
initial compounds which develop oxy-acids with a consider-
able optic activity namely: mandelic acid and α-naphthyl-
glycollic acid. These turn in opposite direction, but belong
to the same configuration series. Figure 1 shows kinetic
curves of the hydrogenation phenyl-glyoxylic acid and of
the dioxime in coordinates: reaction rate versus - time
and rate versus - degree of transformation. Table 1 shows
results of characteristic experiments with regard to the
optical activity. The comparatively high value of the specific
optic activity of the developed diamine is striking. The
results obtained show certain configuration interrelations
between the catalyst and the reacting molecules. In the
cases investigated the protective colloid (gum arabic) does
not seem to act as asymmetric carrier, nor as optically
active solvent. The asymmetric carrier chosen by the authors
has a selective effect during catalysis, since it favors the

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development of an acid with a D-configuration. The above results prove a great configuration correspondence between the asymmetric catalyst (rather the asymmetric carrier) and the spatial structure of the reacting molecule (Ref 13). Special experiments proved that the protective colloid also acts as asymmetric carrier (also Ref 2). The results obtained finally prove that the metal particle is not in the solvate cover of the micelle, but immediately contacts the asymmetric molecule of the protective colloid. The course of an asymmetric adsorption and of such a catalysis thus become possible. There are 1 figure, 1 table, and 13 references, 11 of which are Soviet.

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SOV/20-129-1-28/64

AUTHORS: Balandin, A. A., Academician, Klabunovskiy, Ye. I.

TITLE: Stereochemical Investigation of Active Centers of the Catalyst

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 1,
             pp 102 - 104 (USSR)

ABSTRACT: Conclusions on the structure of the catalytically active cata-
             lyst surface are rendered possible by the investigation of the
             catalysis of molecules with complicated configuration. If the
             size and structure of the reacting molecules is varied, the
             absolute dimensions of centers protruding from this surface
             and their statistical distribution can be determined. Thus
             hydrogeration of the tryptic (I) (2,3-(anthrylene-9',10')-5,6-
             (anthrylene-9",10")-cyclohexene-2-dione-1,4) is of interest
             (see Diagram). (I) was synthesized by condensation of tryptic
             quinone (II) with anthracene by boiling it for 5 hours in an-
             hydrous ethylbenzene. The constants and transformations of (I)
             (Ref 2) are shown. (I) was hydrated under normal atmospheric
             pressure and at 45° over the nickel catalyst skeleton in freshly
             distilled dioxane free from peroxide (see Diagram). The hydro-
Card 1/3   genation product (IV) was recrystallized. Its melting point is

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of the Catalyst

221°, its empiric formula $C_{34}H_{24}O_2$. Figure 1 shows the varia-
tion in the hydrogenation rate of (I) depending on the reac-
tion process, as well as the hydrogenation curve of tryptic
quinone. The investigation of the structures of (I) and (IV)
is difficult. For this reason, apparently, the analysis re-
sults deviate from the theoretical values. Yu. P. Yegorov
plotted the infra-red spectra. They showed an ethylene bond
in the case of (I) which is missing in the hydrogenation pro-
duct (IV). Moreover, the frequencies typical of the O-H bond
are missing in the spectrum of (IV). Hence it appears that no
isomerization of (IV) to a dienediol (V) took place. Hydro-
genation of (I) seems to lead to the formation of dihydro-
diketone (IV) without by-products. Figure 2 gives a schematic
representation of the position of the molecule of compound
(I) on the surface of the catalyst. In connection with the
hydrogenation of such a compound only planar orientation of
the cyclohexenedione ring on this surface seems to be possible.
The height of an active center on the surface where hydrogena-
tion of (I) takes place is determined from the true scale of

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the model of the active complex. The fact that this reaction takes place at all (although at a low rate) indicates that the height mentioned amounts to at least $3.17 Å$. The size of the active center surface can be approximately estimated on account of the distance between the meso positions on the model (Fig 2). It cannot amount to more than $4.8 Å$. The stereochemical model of the intermediate complex discussed here differs considerably from the hydrogenation of tryptic quinone investigated previously. The number of active centers is considerably reduced due to the surface orientation of the molecule and the steric hindrance of the reaction; hence the low rate of reaction. There are 2 figures and 2 references, 1 of which is Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

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SOV/20-129-4-22/68

AUTHORS: Balandin, A. A., Academician, Karpeyskaya, Ye. I., Tolstopyatova, A. A.

TITLE: On the Irreversible Catalysis in the Presence of Metallic Rhenium

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 4, pp 795-798 (USSR)

ABSTRACT: Metallic rhenium, applied to active carbon dehydrogenates the cyclic 6-membered hydrocarbons. On an ammonium perrhenate (Re-1) catalyst small quantities of cyclohexene and also benzene are produced from cyclohexane (Ref 3). This is not the case on a catalyst of a dioxane complex of rhenium-acid-anhydride (Re-2). The authors investigated the transformation of cyclohexene on Re-1 and Re-2 to find the reasons for cyclohexene formation on Re-1. Moreover, the capability of rhenium to bring about irreversible catalysis (expression by N. D. Zelinskiy) was to be investigated. The gaseous reaction products were collected in the gasometer by V. V. Patrikeyev. They consisted of hydrogen with 6-8% methane. The experiments were made between 215° and 465°C. For both catalysts a temperature range was distinctly observable in which no gas is formed and the process takes place according to equation

$3C_6H_{10} = C_6H_6 + 2C_6H_{12}$. At higher temperatures hydrogen is separated.

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On the Irreversible Catalysis in the Presence of   SOV/20-129-4-22/68
Metallic Rhenium

Catalysates of several experiments with Re-1 and Re-2 were poured together. After the removal of the incompletely reacted cyclohexene benzene was chromatographically separated from cyclohexane. Figures 1 and 2 show the results of various experiments which were well reproducible. It may be seen from a comparison of the kinetic data on dehydrogenation[1] of cyclohexene and the disproportionation of hydrogen on Re-1 and Re-2 that the activation energies of the processes are in agreement on both catalysts. Apparently both processes stop at the same stage of reaction. Table 3 shows that on Re-2 benzene is formed from cyclohexene twice as rapidly as from cyclohexane. According to M. Ya. Kagan and N. A. Shcheglova (Ref 6) cyclohexane is dehydrogenated on Pt by 4500 times more slowly than is the transformation rate of cyclohexene. On the basis of these data and according to M. Ya. Kagan and R. M. Flid (Ref 7) the mentioned researchers draw the conclusion that the dehydrogenation of the cyclic hydrocarbons takes place step-wise (see Scheme). The results obtained by the authors are in contradiction with this conclusion: cyclohexane is dehydrogenated on rhenium not according to a step-mechanism but according to a sextet mechanism. Benzene was formed on Re-1 from cyclohexene about twice as rapidly (Table 4.

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On the Irreversible Catalysis in the Presence of   SOV/20-129-4-22/68
Metallic Rhenium

It may hardly be assumed that the dehydrogenation of cyclohexane
on two catalysts of the same chemical properties and on the same
carrier should proceed according to two different mechanisms.
Cyclohexene is no intermediate (in contradiction to the scheme of
references 6, 7) since it was not obtained in the reaction on
Re-2. Cyclohexene thus results from a side-reaction which takes
place to a small degree besides the sextet dehydrogenation. There
are 2 figures, 4 tables, and 8 references, 7 of which are Soviet.

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5(7)

67920
SOV/20-129-5-30/64

AUTHORS: Shcheglova, A. P., Balandin, A. A., Academician, Bogda-
nova, O. K.

TITLE: Kinetics of Dehydrogenation of Isopentenes

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 5,
pp 1071 - 1074 (USSR)

ABSTRACT: In one of their previous papers the authors had dealt with
the investigation of the dehydrogenation kinetics of buty-
lene on a mixed oxide catalyst (Ref 1). Equation (1) holds
for the results obtained (Ref 2). It, however, holds also
for the dehydrogenation of alcohols on an oxide catalyst
(Ref 3). Of late, the catalytic dehydrogenation of isopen-
tenes has been acquiring great practical importance as a
method of producing isoprene for the caoutchouc synthesis.
The authors had earlier (Ref 4) determined the conditions
of isopentene dehydrogenation under dilution with steam on
an oxide catalyst. The same catalyst served for the investi-
gation under review. It was confirmed by special experiments
that steam does not influence the reaction rate on diluting
Card 1/4   the isopentenes (Fig 1). Steam acts in a similar way as the

Kinetics of Dehydrogenation of Isopentenes

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inert gases nitrogen and argon. The principle supporting the method was described in reference 4. Isopentenes were obtained by the dehydrogenation of isoamyl alcohol on aluminum oxide. The experiment was made with the fraction having a boiling temperature at $31-38°$; it contained 2-methyl butene-1 and 2-methyl butene-2. Experiments with pure isopentenes were carried out at $520-600°$. Table 1 shows the results obtained. As may be observed therefrom the reaction runs without the formation of appreciable amounts of decomposition side products. Experiments with isopentenes and isoprene were carried out between 530 and $580°$. These mixtures contained 22.2 mol% of isoprene. Data obtained are given in table 1. On comparing the data obtained from mixtures with those of isopentenes it may be observed that the degree of transformation of the latter into isoprene is much lower in the case of mixtures than with pure isopentenes. Isoprene is adsorbed more strongly on the active centers of the catalyst, and inhibits the reaction. Figure 2 shows the dependence of the relative adsorption coefficient Z_2 of isoprene on temperature, calculated on the basis of formula (2).

Card 2/4   Table 2 summarizes the data concerning the determination of

Kinetics of Dehydrogenation of Isopentenes

Z_3 (relative adsorption coefficient of hydrogen). As may be seen from table 2, $Z_3 = 0.8$ holds and is independent of temperature. Thus, hydrogen is adsorbed on the catalyst almost as strongly as isopentene. On the strength of data obtained, rate constants were determined by the aid of equation (1). At $530°$, $540°$, $560°$, and $580°$ the constants are 4.3; 5.4; 7.7; and 10.7. The corresponding activation energy is 23.3 kcal/mol. Figure 3 shows the dependence between lg k_o and the reciprocal temperature. The points are situated on a straight line. The Arrhenius equation is satisfied. On the strength of the known formulas (Ref 3) the authors calculated the change of free energy, of heat capacity, and of entropy of the adsorptive displacement (Table 3). The authors state that isopentenes are more quickly dehydrogenated than butylenes. Butadiene is more strongly adsorbed on the active centers of the catalyst than isoprene. There are 3 figures, 3 tables, and 4 Soviet references.

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